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REVIEW

The history and development of a rigorous metrological basis for pH measurements

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Abstract This paper discusses the basis and historical development of the traceability chain for pH. The quantity pH, first introduced in 1909, is among the most frequently measured analytical quantities. The practical measurement of the pH value of a sample is inexpensive, easy to perform, and yields a rapid result. However, the problems posed by the traceability of pH are not easy to solve. Most pH measurements are performed by potentiometry, using a glass electrode as the pH sensor. Such pH electrodes must be calibrated at regular intervals. Confidence in the reliability of pH measurements requires establishment of a metrological hierarchy including an uncertainty budget for calibration that links the pH measured in the sample to an internationally agreed and stated reference. For pH, this reference is the primary measurement of pH. A traceability chain can be established that links field measurements of pH to primary buffer solutions that are certified using this primary method. This allows the user in the field to estimate the measurement uncertainty of the measured pH data. As the realization of the primary measurement is sophisticated and time-consuming, primary standards are generally realized at national metrology institutes. A number of potentiometric methods are suitable for the determination of the pH of reference buffer solutions by comparison with the primary standard buffers. The choice between the methods should be made according to the uncertainty required for the application. For reference buffer solutions that have the same nominal composition as the primary standard, the differential potentiometric cell, often called the Baucke cell, is recommended.

Keywords pH · Potentiometry · Metrology · Traceability · Reference standard · Primary measurement · Differential cell

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Introduction

The quantity pH is a measure of the acidity of an aqueous solution. Many chemical and physiological processes are affected by the pH. Since the solubility and bioavailability of substances are each functions of the pH, it is also a critical input quantity for climate modeling. The rate of chemical reactions can be altered by pH. Research in environmental science and in biochemistry has given evidence that the measurement uncertainty in pH forms a central contribution to the uncertainty budget of thermodynamic data as well as of geochemical transport models [1]. The first survey article on pH, published in 1914 [2], mentioned the importance of the hydrogen ion concentration and its measurement in biology.

More than 100 years ago, S. P. L. Sørensen introduced the notation pH as a practical expression derived from the measurement of the hydrogen ion concentration [3].

Today, pH measurements are carried out on a large scale, both at the laboratory level and in industry. In fact, pH is among the most frequently measured analytical quantities. The measurement of the pH value of a sample is inexpensive easy to perform and yields a rapid result. In spite of these advantages, the problems posed by the traceability of pH are not easy to solve. The prerequisite

for mutual acceptance of analytical data is comparability of the results, even if these data are measured by different analysts, using different equipment, and at different times and places [4]. Statements of the measurement uncertainty based on traceability to internationally recognized references are required by regulatory bodies or by international quality standards in general [5].

Most pH measurements are performed by potentiometry. In almost all cases, a glass electrode is the indicating pH sensor. A pH electrode used in the field must be calibrated at regular intervals.

Confidence in the reliability of measurement results requires establishment of a metrological calibration hierarchy linking the quantity in the sample to a unit in the International System of Units (SI) or, where this is not possible, to another international agreed and stated reference.

For pH, the result of a calibration must be compared with the value provided by a certified reference buffer solution. The pH value of the reference buffer solution and its uncertainty are assigned using a measurement procedure that itself also must be calibrated. In this way, a traceability chain can be established linking the pH measured in the field to the pH of a primary buffer solution. Primary measurement standards and primary measurement procedures are typically realized by National Metrology Institutes (NMI) in their respective countries.

In the following, the basis and the historical development of the traceability chain for pH is described.

The concept of pH

In the last decade of the nineteenth century, Arrhenius introduced the ionic theory [6]. This theory provides the fundamental relationship between hydrogen and hydroxyl ions and offers the possibility to determine the dissociation constant of water.

In 1904, Friedenthal prepared 14 solutions of known hydrogen concentration and examined the color change of indicator dyes corresponding to a particular hydrogen ion concentration. Friedenthal for the first time established a scale of acidity [7].

In 1909, Sørensen, a coworker of the Carlsberg Laboratory in Copenhagen, defined pH in terms of the concentration with a scale of 0–14 (at 25 °C) derived from the ionic product of water [3]. In the same year, the glass electrode was applied to acidimetric titrations for the first time by Haber and Klemensiewicz [8].

Sørensen's original intention was to simplify the inconvenient figures that result from measurements of the hydrogen ion concentration. Sørensen proposed to take the decadic logarithm of the hydrogen ion concentration multiplied by (−1) and called it "pondus Hydrogenii". Some years later, the concept of activity was introduced [9], and in 1923, Debye and Hückel published [10] the theory of interionic interaction. On the basis of this knowledge, Sørensen and K. Linderstrøm-Lang [11] proposed the definition of pH generally accepted today, which is based on the activity of the hydrogen ions in solution:

$$\mathrm{pH} = -\log a_{\mathrm{H}} = -\log\left(m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^{0}\right). \quad (1)$$

In Eq. 1, a_{H} is the molality-based activity; γ_{H}, the molal activity coefficient of the hydrogen ion H^{+} at the molality m_{H}; and m^{o} is a standard state, chosen to be equal to 1 mol kg^{-1}.

The single ion activity involved in Eq. 1 cannot be measured unambiguously. It is necessary to introduce a convention based on approximations that are related to measurable quantities, to approach the definition of pH as closely as possible.

Since its introduction by Sørensen, the interpretation of the quantity pH has given rise to intense discussion and controversies. Bates, in 1948, stated that "several scales, all masquerading under the name pH, are in common use. Many investigators are thinking and computing in terms of one definition and measuring a different quantity" [12].

Several pH scales have been described which are characterized by standard buffer solutions with assigned pH values [13].

In the 1960s, Bates and co-workers at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology, established the so-called multipoint pH protocol after extensive studies of buffer solutions and suitable electrochemical cells [14]. In the multipoint pH protocol, each pH standard is a dilute aqueous solution with an ionic strength, $I \leq 0.1$ mol/kg. The pH values of these standards are measured using a cell without liquid junction, the so-called Harned cell [15, 16], described below in further detail. This protocol was recommended in 1979 by the International Union of Pure and Applied Chemistry (IUPAC) [17].

In addition to the Harned cell, the 1979 IUPAC Recommendation also presented an operational definition of pH. The pH of an unknown solution, pH(X), in a cell containing hydrogen and a reference electrode with a liquid junction was related to the pH of one standard solution, pH (S), by Eq. 2:

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{[E(\mathrm{S}) - E(\mathrm{X})]F}{RT\ln 10}. \quad (2)$$

In Eq. 2, the quantities E(S) and E(X) are the potentials of this cell containing the standard solution and the unknown sample; and pH(X) and pH(S) denote the pH of the unknown solution and the standard, respectively. The quantities R, T, and F represent the gas constant; thermo-

dynamic temperature, and the Faraday constant, respectively. The quantity RT ln10/F is often referred to as the thermodynamic or Nernstian slope, k. Equation 2 has a major shortcoming: it excludes the contribution from the liquid junction potential (LJP). The LJP arises at the liquid junction between the reference electrode and the solutions S or X and is a complex function of the solution composition and other factors. The difference in the residual LJP between solutions S and X is a fundamental source of bias in the operational measurement of pH. Thus defined, the quantity pH is a number. It was allowed, "to a good approximation," to replace the hydrogen electrodes in both cells by other hydrogen-ion-responsive electrodes, e.g., glass or quinhydrone [17].

In 1981, the British Standard Organization (BSI) recommended [18] a so-called single-standard scale. The pH of a single reference standard, a solution of potassium hydrogen phthalate with a molality of 0.05 mol/kg, was measured in a cell without liquid junction. The resulting pH was defined as a fixed reference point. The pH values of other solutions in the BSI protocol were defined by the operational definition as realized in a cell with a specified geometry of the liquid junction.

These two definitions of "pH" coexisted for a time. During this period, all attempts to harmonize the pH scale recommendations [19] were without success.

In 1985, the IUPAC issued a recommendation, "*Definition of pH scales, standard Reference values, measurement of pH and related terminology*" [20]. This proposal was edited as a "compromise recommendation" and recognized the validity of both the NBS and BSI approaches. This situation was highly unsatisfactory. The application of two pH scales in parallel resulted in two possible pH values for each unknown solution.

The 1985 IUPAC Recommendation was seen as an interim document from the beginning. The recommendation of two incompatible protocols for pH was to be replaced by amended recommendations when "a thermodynamically and metrologically sound pH scale can be recommended" [21]. In the 1990s, pH measurement was one of the first topics addressed in the application of metrological principles to chemistry [22]. The issuance of a new IUPAC document became a necessity, owing to several additional metrological shortcomings of the 1985 IUPAC Recommendation. Notably, the 1985 Recommendation did not address the uncertainty of pH measurements, a topic of increasing importance with the introduction of metrological principles to the field. Also, various different pH definitions and recommendations to measure pH had been uncovered by a critical analysis of the document by F. G. K. Baucke [23]. Baucke, at that time Chairman of the DIN Committee Technical pH measurement was one of the initiators of a Working Party on pH which was established in 1997 [24]. The task for this Working Party was to prepare amended recommendations to replace the 1985 document. After extended deliberations, in 2002, the IUPAC issued a new "Recommendation for a Primary Measurement Procedure for pH" [25]. This document eliminated the "dual pH scale" of the 1985 document and today forms the basis for the primary measurement of pH.

The primary method for the measurement of pH

As presented, in the 2002 Recommendation, the primary procedure for pH is based on the measurement of the potential difference of an electrochemical cell without liquid junction, involving a selected buffer solution, a platinum hydrogen gas electrode, and a silver/silver chloride reference electrode, in cell I [26]:

$$\mathrm{Pt|H_2|buffer, Cl^-|AgCl|Ag.} \qquad \text{Cell I}$$

Cell I was originally developed by Harned and co-workers in the 1930s [15] and is frequently called the Harned cell. Harned originally applied cell I to the determination of activity coefficients. Subsequently, Hamer and Acree at the NBS suggested the use of cell I in accurate pH measurements [27]. This work was developed further at the NBS by Bates [28] and by Hamer and Acree [29] starting in the 1940s.

The principle of cell I is shown in Fig. 1.

Chloride ions are added to the chloride-free buffer at several chloride molalities in order to stabilize the potential of the silver/silver chloride electrode. The Harned cell avoids the liquid junction potential and its associated difficulties. The cell potential consists merely of the difference in the two electrode potentials.

In addition to the use of a cell without liquid junction, a convention is necessary to obtain the single ion activity embodied in Eq. 1 above. The primary method for pH uses

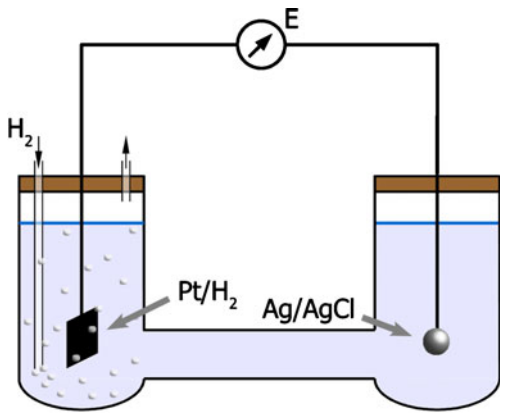

Fig. 1 Platinum, hydrogen | silver, silver chloride cell (so-called Harned cell) for primary pH measurements

the Bates–Guggenheim convention [30]. Bates and Guggenheim suggested this approximation for the single ion activity coefficient based on the Debye–Hückel theory of strong electrolytes. This convention is restricted to solutions of low ionic strength, $I \leq 0.1$ mol kg^{-1}.

The potential difference E of cell I (corrected to 101325 Pa partial pressure of hydrogen) depends on the hydrogen ion activity, a_H, according to Eq. 3:

$$E = E^0 - k \log\left(a_H/m^0\right)\left(m_{Cl}\gamma_{Cl}/m^0\right). \quad (3)$$

In Eq. 3, E^0 denotes the standard potential of the Ag/AgCl reference electrode, m_{Cl} and γ_{Cl} the molality and activity coefficient of the chloride ion. Equation 3 is the well-known Nernst equation applied to the Harned cell.

A pH measurement of a buffer solution using cell I usually consists of different steps [31]. In the first step, E^0 of the silver/silver chloride electrode is determined in a Harned cell filled with hydrochloric acid of fixed molality. The mean activity coefficient of HCl, $\gamma_{\pm HCl}$, at various temperatures is best known at the molality 0.01 mol kg^{-1} [32].

In the second step, the Harned cell is filled with the buffer solution whose pH value is to be measured. A new quantity, the acidity function, pa, is defined by Eq. 4:

$$pa = -\log\left(a_H\gamma_{Cl}/m^0\right). \quad (4)$$

Equations 3 and 4 can be combined to yield Eq. 5, in which pa is a function only of measurable quantities:

$$pa = \left(E - E^0\right)/k + \log\left(m_{Cl}/m^0\right). \quad (5)$$

In the primary procedure for pH, pa is measured as a function of m_{Cl}.

The third step is the extrapolation of the acidity function to zero chloride molality. This extrapolation yields the acidity function corresponding to zero chloride molality, pa_0:

$$pa_0 = -\log\left(a_H\gamma_{Cl}/m^0\right)_{m_{Cl}\to 0}. \quad (6)$$

The value of pa_0 is determined by linear extrapolation of pa as a function of the chloride molality, using measurements at least three values of m_{Cl} in the range from 0.005 to 0.02 mol·kg^{-1}. It is assumed that a linear extrapolation is appropriate if the change in ionic strength produced by the addition of chloride is restricted to less than 20%.

This extrapolation is mathematically depicted in Eq. 7, where b is an empirical, temperature-dependent constant:

$$pa = pa_0 + bm_{Cl}. \quad (7)$$

In the fourth step, the activity coefficient at the ionic strength I of the buffer, γ_{Cl}, is obtained by adopting the Bates–Guggenheim convention. The value of γ_{Cl} is given by Eq. 8:

$$\log\gamma_{Cl} = -A\left(I/m^0\right)^{1/2}/\left(1 + 1.5\left(I/m^0\right)^{1/2}\right). \quad (8)$$

In Eq. 8, A is the Debye–Hückel temperature-dependent limiting slope [33].

Finally, the pH value of the primary pH buffer solution, pH(S), is calculated by combining Eqs. 6, 7, 8, and the definition of the pH, Eq. 1, to yield Eq. 9.

$$pH(S) = pa_0 + \log\gamma_{Cl}. \quad (9)$$

Traceability of the measured pH value to the SI can be established for pH(S) values determined as described above if the expanded uncertainty associated with the extra-thermodynamic assumption, the Bates–Guggenheim convention, is taken into account. Unfortunately, the measurement uncertainty contribution arising from the use of this convention is 0.01 (expanded measurement uncertainty, coverage factor k=2). In comparison, the experimental expanded measurement uncertainty (k=2) obtained for a pH value of a typical primary buffer solution is 0.003 to 0.004. Values of pH that include all sources of uncertainty excepting that of the Bates–Guggenheim convention, as is the common practice at most NMIs, are considered conventional pH values, which is sufficient for most applications [21].

Primary pH reference buffers

The primary buffer solutions currently recommended by IUPAC establish the so-called multipoint pH protocol [14]. The primary method for pH is used by the NMIs to assign pH values to a restricted number of primary reference solutions in dilute aqueous solutions between pH 3 and 10 and in a temperature range from 5 °C to 50 °C. Typical values of the pH of primary reference buffer solutions as listed in the 2002 IUPAC Recommendation [25] and also in the ISO [34] are listed in Table 1.

Several criteria must be fulfilled for a material to qualify as a primary pH buffer material. Primary buffer materials must be available at high purity, have high stability, and good reproducibility of preparation. The buffer solutions themselves have been selected such that only small liquid junction potentials occur in measurements made with practical pH electrodes incorporating liquid junctions. Of course, the magnitude of the residual liquid junction potential also depends on the kind of liquid junction device (diaphragm) used.

Each batch of material must be individually certified. The pH and the associated uncertainty are given in the certificate for each measurement temperature. Batch to batch variations are of the same order as the expanded measurement uncertainty of the primary method.

Calcium hydroxide and potassium tetraoxalate are also certified using the above primary measurement procedure.

Table 1 Typical values of pH for primary reference buffer at 25 °C

Primary pH reference buffer	Molality in mol kg^{-1}	pH, typical values at 25 °C [25]
Potassium hydrogen tartrate	Saturated at 25 °C	3.557
Potassium hydrogen phthalate	0.05	4.005
Potassium dihydrogen phosphate/ disodium hydrogen phosphate	0.025/0.025	6.865
	0.008695/0.03043	7.416
Sodium tetraborate decahydrate	0.01	9.180
Sodium bicarbonate/sodium carbonate	0.025/0.025	10.012

These figures should not be used in place of the certified value for a specific batch of buffer material

They are also listed, e.g., in the DIN 19266 [35]. However, they are not recommended by IUPAC as primary buffers, because the contribution of the hydroxyl or hydrogen ion to the ionic strength is significant.

The Differential pH Cell (Baucke Cell)

Operating the Harned cell is very sophisticated and time-consuming. In general, primary measurement standards are realized by NMIs. In many cases, these standards are not economically suitable for calibration and reference laboratories or for routine measurements. There are a number of cells having liquid junctions which may be used for the determination of the pH of a secondary reference buffer solution by comparison with a primary buffer solution [36]. Standardization of a secondary buffer solution (often by a non-NMI entity) extends traceability to a greater market and offers significant economic advantages.

For reference buffer solutions with the same nominal composition as that of the primary standard, the differential potentiometric cell is recommended. Baucke was the first to apply [37–39] a differential cell, cell II, to the standardization of pH buffers:

$$\mathrm{Pt(1)|H_2|\ buffer\ S_1||buffer S_2|H_2|Pt(2).} \qquad \text{Cell II}$$

Cell II consists of two identical Pt|H_2 electrodes, Pt(1) and Pt(2); and two quasi-identical buffers, S_1 and S_2, with pH values, pH(S_1) and pH(S_2). A diaphragm, ||, separates S_1 and S_2. The cell is constructed such that the H_2 pressure, p_{H2}, at Pt(1) and Pt(2) is identical. The cell is schematically shown in Fig. 2.

The potential, $E_{\text{cell II}}$, of cell II is given by Eq. 10:

$$E_{\text{Cell X}} = E(2) - E(1) + E_j. \tag{10}$$

In Eq. 10, $E(1)$ and $E(2)$ denote the potentials of Pt(1) and Pt(2), respectively. E_j is the liquid junction potential that forms between S_1 and S_2 at the diaphragm. The correction of $E(1)$ and $E(2)$ to standard pressure cancels in Eq. 10, as p_{H2} at Pt(1) equals p_{H2} at Pt(2).

Equation 10 may be rearranged and expressed in terms of pH:

$$\mathrm{pH}(S_2) = \mathrm{pH}(S_1) - \frac{E_{\text{Cell II}} - E_j}{k}, \tag{11}$$

The substitutions in Eq. 11 of pH(S_1) and pH(S_2) for $-E(1)$ and $-E(2)$ are based on the thermodynamic response of the Pt|H_2 electrode (Nernst equation) to a_H and on the notional definition of pH (pH=−log a_H) [25].

Provided that S_1 and S_2 are quasi-identical in composition, $|\mathrm{pH}(S_2)-\mathrm{pH}(S_1)|\leq 0.02$, and $3<\mathrm{pH}<11$, measurements [39] indicate that Eq. 12 holds:

$$|E_j| < 0.1|E_{\text{Cell II}}|. \tag{12}$$

In other words, if these three conditions are fulfilled, the bias associated with E_j in cell II is less than 10% of $E_{\text{Cell II}}$, and pH(S_2) may be calculated using Eq. 13 (i.e., neglecting E_j):

$$\mathrm{pH}(S_2) = \mathrm{pH}(S_1) - \frac{E_{\text{CellX}}}{k}. \tag{13}$$

The uncertainty associated with the use of Eq. 13 may be estimated from Eq. 12.

Cell II is used to assign pH(S_2) for a certified reference material (CRM) as follows. S_1 is a primary pH buffer, with pH(S_1) having been determined previously using a Harned

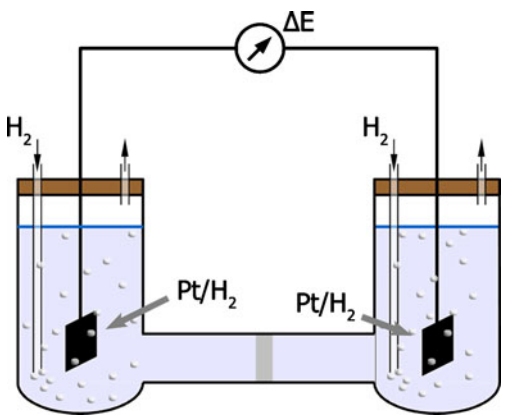

Fig. 2 Differential potentiometric cell (Baucke cell)

cell measurement [25]. S_2 is a CRM buffer, for which pH (S_2) is to be assigned. Typically, S_1 is a small batch reserved as a primary reference only, and S_2 is a large batch with the same nominal composition as S_1. The source reagent(s) for S_2 and those for S_1 usually derive from different lots. The traceability of pH(S_2) for the CRM to the SI is via the differential measurement from pH(S_2) to pH (S_1) and the Harned cell measurement from pH(S_1) to the SI. The contribution associated with Eq. 12 to the overall uncertainty is negligible.

Cell II is frequently referred to as the "Baucke cell." Owing to the simplicity of the measurement as compared with the primary measurement of pH (Harned cell), the Baucke cell has been adopted by a number of countries [40, 41] in their scheme for the dissemination of pH measurement capability.

Routine pH measurements: the glass electrode

Owing to their complexity and restriction to specific buffers, the primary and differential methods described above are used at NMIs and calibration laboratories to realize and disseminate the quantity pH.

This section briefly outlines the methodology for routine pH measurements, including contributions of Baucke to this field.

Routine pH measurements are generally performed using a pH measuring setup composed of a pH meter and a pH electrode. The pH electrode, often misleadingly called a "glass electrode", in fact comprises two separate electrodes: the glass electrode proper and an external reference electrode with a liquid junction (diaphragm). The electrode pair is generally designed as a combination or single rod. A typical pH electrode can be represented by Cell III:

$$\mathrm{Ag|AgCl|KCl||sample,\ buffer|glass|internal\ buffer(pH\ 7)} + \mathrm{KCl|AgCl|Ag} \qquad \text{Cell III}$$

The Ag|AgCl reference electrode and the KCl solution (3.0 $mol \cdot L^{-1}$ to 3.5 $mol \cdot L^{-1}$) on the left side of cell III comprise the external reference electrode. The diaphragm || between the KCl solution and the sample buffer provides electrical contact while minimizing flow of the KCl solution into the sample buffer. An LJP arises at this boundary of solution phases.

Owing to various random and systematic effects, notably including the LJP, cell III must be calibrated with respect to reference buffer solutions traceable to primary pH standards.

The calibration procedures can be subdivided into single-point, two-point, and multipoint calibrations [25]. In each of these calibration procedures, the uncertainties of the buffer pH values (see preceding sections) and the residual liquid junction potential must be included in the calculation of the uncertainty of the pH of the sample.

Single-point calibration uses one standard. The calibration function is assumed to be a straight line defined by the measured potential of the standard and the thermodynamic (Nernstian) slope, k. Single-point calibration is of primary interest to obtain an approximate pH value prior to a more precise measurement using two-point or multipoint calibration. The two-point or bracketing procedure is used in most

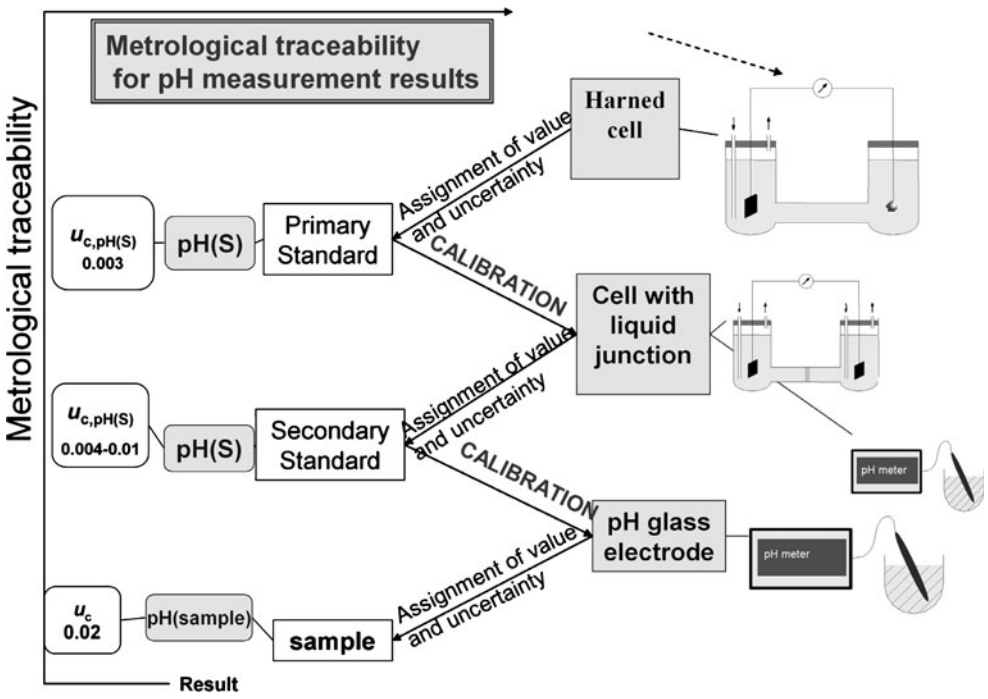

Fig. 3 Metrological traceability scheme for pH according to [42]. U_c denotes the expanded measurement uncertainty (coverage factor k=2) assigned to the pH values

routine pH measurements. This calibration uses two standards with values that "bracket" the range in which the unknown lies.

Multipoint calibration [25, 42] is recommended when minimum uncertainty and maximum consistency are required over a wide range of pH(X) values. The pH values of reference buffer solutions which differ in composition and buffer capacity from the primary standard buffers are also determined by a multipoint calibration. These pH reference buffers often called technical or ready-to-use buffer. The calibration of the electrode is calculated from linear regression of the difference in the cell potential at each of the calibrant pH values from the least-squares line.

In both the two-point and multipoint calibration protocols, the glass electrode typically yields a practical slope, k' that is slightly smaller than k. The main factor in this deviation is variation in the LJP with pH [25]. However, by comparing the response of glass and $Pt|H_2$ electrodes, Baucke et al. [43] demonstrated that a portion of this deviation to all appearances results from changes in the surface activity of silanol groups on the surface of the glass membrane and is, thus, an inherent property of the glass electrode itself.

Conclusion

Established traceability structures are the prerequisite for the global comparability of measurement results. Also due to the persistent work of F.G.K. Baucke within the IUPAC Working Party on pH, a metrologically well-founded primary method for pH is now widely adopted in national [44] and international [45] standards. The use of a simple differential potentiometric cell to derive secondary pH buffer solutions with the same chemical composition as the corresponding primary buffer, as conceived by Baucke, has been implemented at many calibration laboratories, as well as at several NMIs in developing countries.

Figure 3 depicts a traceability scheme for pH according to [46]. The expanded uncertainty U_c is obtained by multiplying the standard uncertainty by the coverage factor $k=2$. Normally, the pH value lies with a probability of approximately 95% within the assigned interval of values [49]. At the secondary level, using the differential pH cell for calibration, the expanded uncertainty of the resulting pH is in the same order as for the primary method. These reference buffer solutions are used in general to determine pH values of buffer solutions with composition different from the primary pH buffers with a pH glass electrode. An expanded uncertainty of 0.01 is assigned to these pH values. The difference in uncertainty is caused by the contribution of the residual liquid junction potential to the overall uncertainty. The expanded uncertainty assigned to the pH of the sample is therefore in the order of 0.02 for most applications.

The work on the traceability and dissemination of pH is not yet complete. The Bates–Guggenheim convention is only valid at ionic strengths up to 0.1 mol kg^{-1}. For applications in clinical chemistry and in environmental samples (e.g., rainwater, seawater), pH reference buffer solutions with ionic strengths more similar to these samples are expected to improve the comparability of measurement results in these matrices. Further investigations into solution theory and into the concept of single ion activity are necessary to overcome present limitations for the primary procedure for measurement of pH.

Finally, the dissemination of traceability from the NMI to the user in the field is also an area of activity. A new IUPAC project: "Comparable pH measurements by metrological traceability for improving the scientific basis and broadening the applicability of pH measurement" [47] is developing applicable recommendations. Project 843 of EURAMET (European Association of National Metrology Institutes) gives recommendations for the calibration and evaluation of pH on site measuring instruments [48].

These activities all continue to build on work originally conceived and implemented by F.G.K. Baucke.

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